Chemical Crystallography
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Lecture – 34
Systematic Absence Conditions from Special Structure Factor Expression

Welcome back to the course of Crystallography. In the previous lecture we have discussed about the Structure Factor, Expression of structure factor in various forms. And then we have seen how one can derive or how can one can understand the relationship between the structure factor F h k l with the rho xyz, which is nothing but the electron density associated with every xyz.

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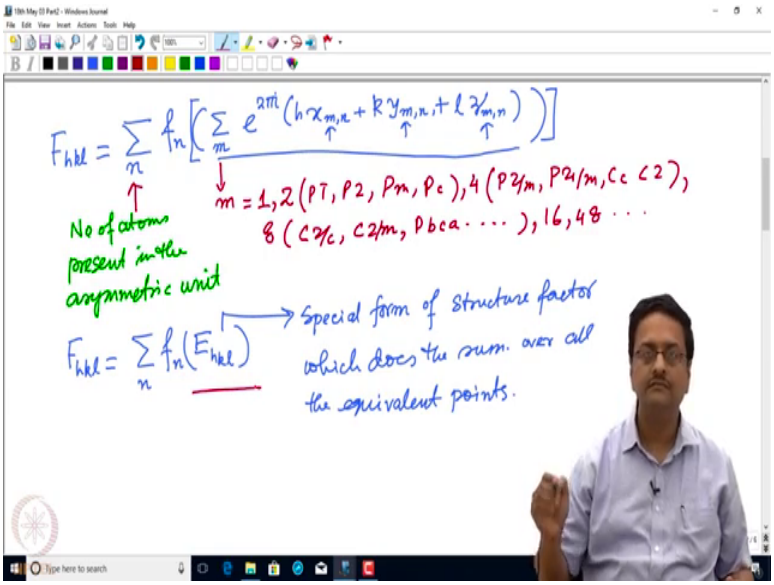

And in the previous lecture we have also shown that the structure factor is a Fourier transform of the electron density, and electron density is a Fourier transformation of structure factor. From there we derived the special structure factor information or special structure factor expression which is written as E h k l. And then from there we try to derive the expressions for different symmetry operations in present in x ray present in a lattice.

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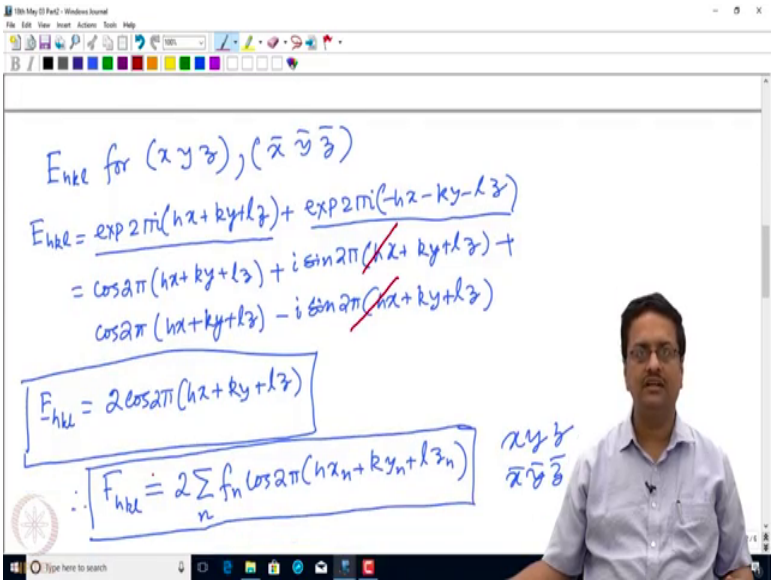

So, we have seen it for the centrosymmetric lattice crystal where you have equivalent points x y z and x bar y bar z bar.

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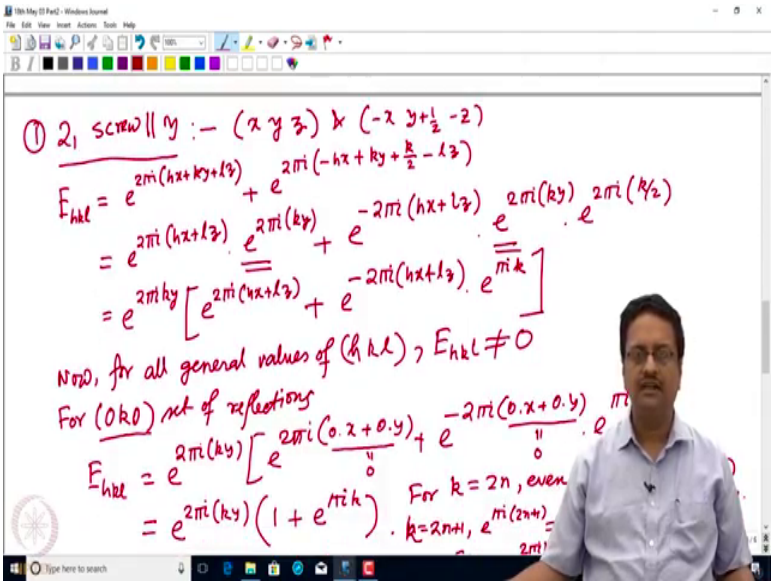

And then we have derived the systematic absence conditions for 2 1 screw parallel 2 y, and then n light parallel 2 y.

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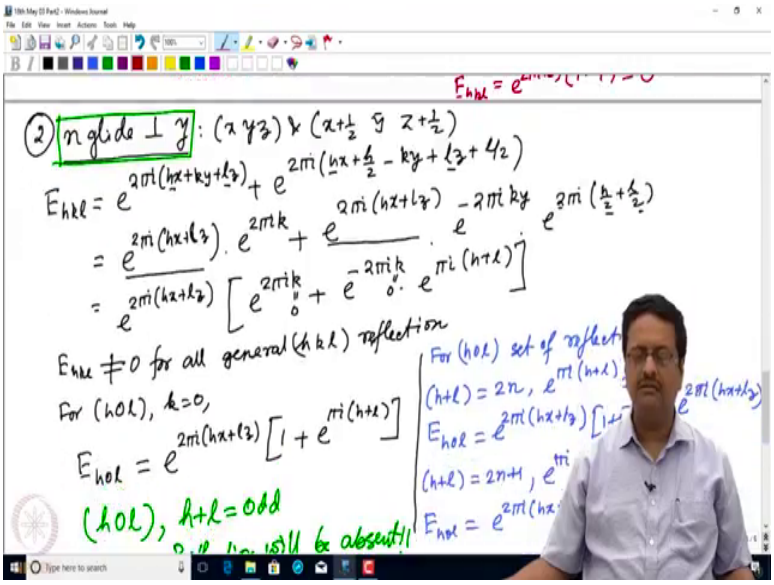

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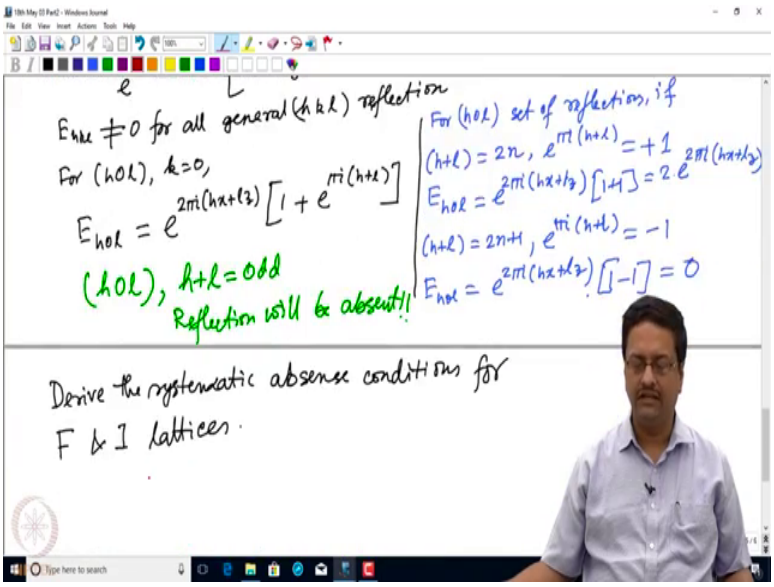

And I left you with the assignment where I wanted you to determine the systematic absence conditions for I lattice and F lattice.

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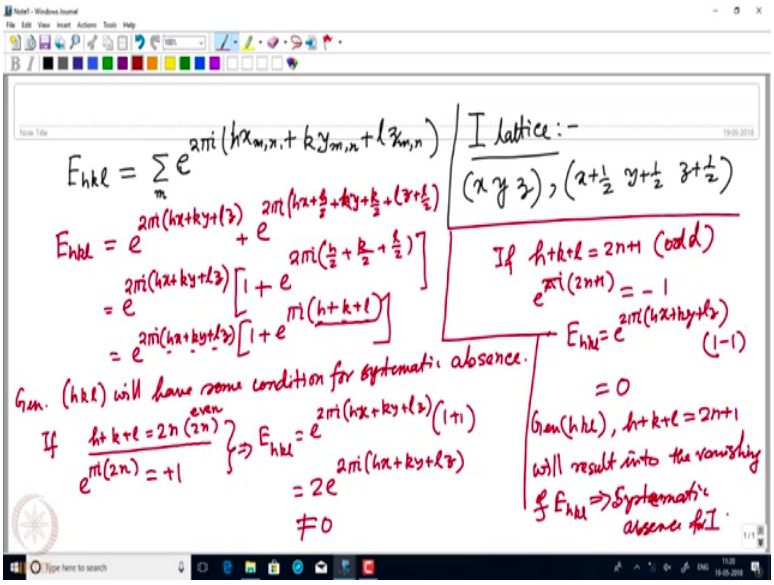

So now, from there let us start. As you can recall that when we are trying to calculate this special structure factor expression E x y z, sorry E h k l we are actually calculating a special structure factor expression E h k l we are doing a sum over m e to the power 2 pi i h x m n plus k y m n plus l z m n.

Where m represents the symmetry related equivalent points. So, what we need to do is, for any systematic absence condition derivation, we need to first write down the corresponding equivalent points for that particular symmetry. So, for example, in case of a body centered lattice, I lattice we have atoms at xyz, that is associated with the corners, and the atom associate at present at the center of the unit cell which is x plus half, y plus half, z plus half.

So now, if we try to write the expression for E h k l for these 2 equivalent points, we can write it as e to the power 2 pi i hx plus ky plus l z; plus e to the power 2 pi i hx plus h by 2 plus k ky plus k by 2 plus l z plus l by 2.

So now, if we take e to the power 2 pi i hx plus ky plus lz out, what we have is 1 plus e to the power 2 pi i h by 2 plus k by 2 plus l by 2. Which means, it is equal to e to the power 2 pi i hx plus ky plus lz into 1 plus e to the power pi i h plus k plus l. Now here you see that the first term contains all the 3 h k and l and the exponential here also has terms h k and l.

So, by looking at this we can understand we can conclude that the systematic absence condition that will arrive for this particular symmetry that is I centering will be for

reflects general inflections h k l. So, general reflections h k l will have some condition for systematic absence.

So now there may be 2 situations with the sum h plus k plus l. If h plus k plus l is even, then e to the power pi i and even number is equal to plus 1. So, this would mean that E h k l is equal to e to the power 2 pi i hx plus ky plus lz into 1 plus 1 which is equal to 2 into e to the power 2 pi hx plus ky plus lz; which is not equal to 0. So, that means, h plus k plus l even the reflections are going to be present.

What happens if we have the other condition when if h plus k plus l is 2 n plus 1 which means odd? Then e to the power pi i 2 n plus 1 is going to be minus 1 so; that means, E h k l is going to be equal to e to the power 2 pi i hx plus ky plus lz into 1 minus 1 which is equal to 0. That means, for general h, k, l reflections h plus k plus l as 2 n plus 1 will result into the vanishing of E h k l.

Hence will it correspond to the systematic absence for i. So, the condition for systematic absence for a body centered lattice is for general reflections h k l, h plus k plus l odd. So now, let us see the same for the F centered lattice.

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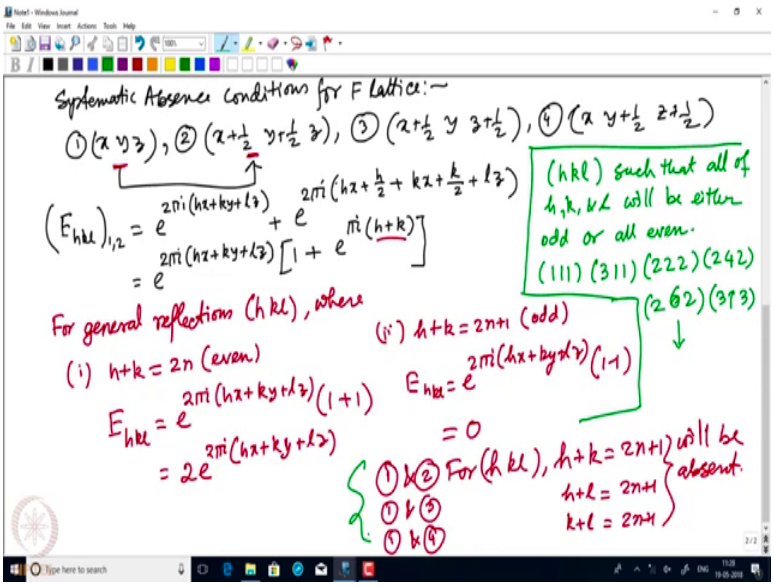

So, systematic absence conditions for F lattice. Once again we need to first write down the equivalent points corresponding to F lattice. This is the corner points, and then the other face centered atom positions are x plus half, y plus half to z. Third point is x plus

half y z plus half and 4th point is x y plus half z plus half. So now, if we first apply and try to calculate the systematic absence condition for the point 1 and 2 we should write E h k l between point 1 and 2 is nothing but e to the power 2 pi i hx plus ky plus lz plus e to the power 2 pi i h x plus h by 2 plus kx plus k by 2 plus lz.

So, now if I take e to the power 2 pi i hx plus ky plus lz out, what we get is, 1 plus e to the power pi i h plus k. So now, here on inspection what we can see is that, the term inside the bracket has h plus k, it does not contain l. So, the systematic absence condition which will result for this 2 points which are point number 1 and point number 2 will be based on h and k being non 0. So now, in this case for general reflections h, k, l where condition 1 h plus k is 2 n, that is even.

E h k l is e to the power 2 pi i hx plus ky plus lz into 1 plus 1 as before. So, it is equal to 2 t to the power 2 pi i hx plus ky plus lz. For condition 2 where h plus k is equal to 2 n plus 1 which means odd. The same E h k l like before it will become hx plus ky plus lz into 1 minus 1 will become equal to 0.

So, the systematic absence condition for point number 1 and 2 will be for general h, k, l set of reflections, h plus k equal to 2 n plus 1 will be absent. Similarly, if we do the same for 1 and 3 we will see that h plus l equal to 2 n plus 1 will be absent. If we do the same for 1 and 4, we will see that k plus l equal to 2 n plus 1 will be absent. That means, for a face centered lattice, all these 3 conditions should be simultaneously satisfied, then only we will say that there is a face centered lattice. What does it actually mean? It actually means in case of face centered lattice, the reflections that will be systematically present are going to have h, k, l such that all of h, k and l will be either odd or all even.

So, the face centered lattice will have only reflections where it is like 1 1 1, 3 1 1, 2 2 2, 2 4 2, 2 6 2, 3 1 3 etcetera. Well, all the h, k and l are either all odd or all of them are even only in those cases you do any summation of h plus k or h plus l or k plus l. In all those cases the sum will be even now. If one of those is even and other 2 are odd immediately, it means that for that particular reflection. The conditions that are for face centered lattice is not satisfied, then it will it is not a face centered lattice. So now, let us try to see the; So now, let us try to see the schematic diagram for the structure solution experiment for a x ray diffraction experiment.

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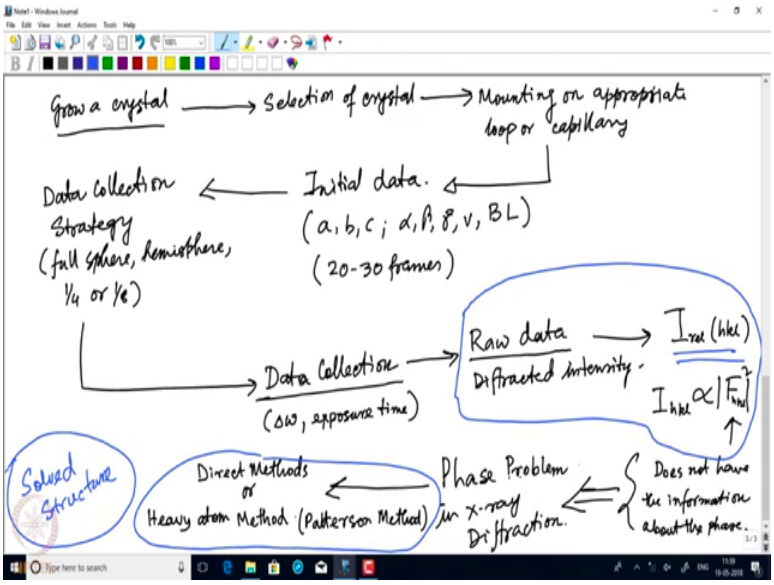

So, what we are doing we are we first need to grow a crystal? Then we do a selection of crystals, then we do a mounting on appropriate, on appropriate look or capillary, and then we collect initial data.

So, this initial data then gives us information about the unit cell parameters, volume and the corresponding Bravais lattice information as well. So, this is done with a very limited number of data maybe about 20 to 30 frames, or 20 to 30 images. And then from there we determine a data collection strategy whether we need a full sphere data or a hemisphere or of the quadrant or of 10 data.

So, then what we do is we collect the data. So, in this data collection methodology what we have? We need to decide the exposure time we need to decide the delta omega that is the width of data that we would like to do. So, we need to decide whether we want to do is; small width or a large width so, delta omega exposure a time, all these we need to worry about it at this point.

So, from this data collection after we have obtained the in extra intensities, the job becomes difficult. What happens is that the diffracted intensities from a crystal depends on a large number of factors. So, after data collection what we get is the raw data which is nothing but the diffracted intensities, diffracted intensities from a large number of reciprocal lattice points that is a large number of crystallographic planes. And these intensities we will have a large radiation in their number; that is the intensity of some

reflections will be very high, intensity of some reflections will be very low, because of the difference in the planar density on those planes which are responsible for diffraction.

So, this raw data has to be then treated, in such a way that this raw data is converted to a standard experimental data which then can be used by any structure solution program. See the raw data can have variable intensity for a given crystal suppose I take one crystal and do the data collection with a seal tube x ray source which has very low intensity, then we take the crystal to a facility where we have a micro focus source which has about 10 times more intensity. Then we take the same crystal to a rotating anode source which might have about 70 80 times more intensity from compared to the, seal tube source.

And then you take it to the synchrotron which has much more intensity. So, when the intensity of the incident radiation is changing drastically. The diffracted beam intensity changes simultaneously. Then depends what temperature at which we are collecting data. If we are collecting data at room temperature, we will have a certain intensity; because at room temperature all the atoms molecules are vibrating at a given x y and z width.

So, the electron density associated with every atom is diffused over a range on a particular h, k, l plane. And the intensity of diffraction is then less. When you cool a crystal 200 Kelvin temperature at that point the vibration is much reduced. So, the electron density is more confined to a particular atom, as a result the beam intensity increases. Now even if we use one crystal and then collect the data with different exposure times or different width and all that the intensity of the diffracted beams will be different.

So, one has to apply a large number of corrections to this raw data to be able to use it for a structure solution program. So, this raw data is then converted to some I relative for every h, k, l by applying some corrections, and as I we know that the I h k l is proportional to modulus of F h k l square. One can then convert the intensity to the corresponding structure factors, and use it for structure solution purpose.

So now this F h k l the mod of F h k l does not have the information about the face. Because what we are measuring from a diffraction data is just the intensity of the diffracted beam, and we have no means to measure the face of each one of those reflections. So, when we are converting the intensity to a structure factor, we are only

getting the structure factor amplitude. We are not getting the phase information of the structure factor.

So, this problem that we always encounter is called the phase problem in X-ray diffraction. So, this phase problem is then solved by different methods. There are different methods called that a set of direct methods. So, this then we use different packages to solve the phase problem.

We use direct methods or if our structure or if our compound has any heavy element, we use the heavy atom method which is named after Patterson as Patterson method. So, in we coming lectures we will discuss about the features which I have mart here, the treatment of raw data and to generate the I h k ls from the raw data. And then how do we solve the phase problem using 2 different methods?

So, these 2 are most important steps in x ray diffraction practice where after data collection you need to spend a lot of time to do a proper data handling. Improper data handling will lead to incorrect intensities. And if you have incorrect intensities for whatever reason, the structure solution using direct methods the Patterson method is going to fail; because those are highly dependent on the I relatives or from that whatever structure factor amplitude that we are calculating. They are all dependent highly dependent on the structure factor amplitude.

So, today we have discussed about the systematic absence conditions generated for I and F centered lattices. I hope now you will be able to do it for all other symmetry elements and symmetry operations, then we just discussed about a flow chart of X ray diffraction experiment; where you start from growing a crystal and then reach slowly one by one to the structure solution. So, by direct method what we end up is the solved structure.

This solved structure is the raw solved structure, which then need to be refined using least square refinement methods. So, that will be another portion of this lecture where we will talk about the least square refinement of solved structures. There we will discuss about a number of parameters like R factors, w R 2 goodness of fate and so on.